Improvement of the lubrication properties of grease with Mn_3O_4 /graphene ($\text{Mn}_3\text{O}_4\#\text{G}$) nanocomposite additive

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Abstract: Although grease can effectively lubricate machines, lubrication failure may occur under high speed and heavy load conditions. In this study, Mn_3O_4 /graphene nanocomposites ($\text{Mn}_3\text{O}_4\#\text{G}$) were synthesized using a hydrothermal method as lubricant additives. The lubrication properties of compound grease with $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposite additive under heavy contact loads of 600–900 N (3.95–4.59 GPa) were investigated. First, the nanocomposites were dispersed into L-XBCEA 0 lithium grease via successive electromagnetic stirring, ultrasound vibration, and three-roll milling. Compound grease with additives of commercial graphene (Com#G) was also investigated for comparison. Tribological test results revealed that the trace amounts of $\text{Mn}_3\text{O}_4\#\text{G}$ (as low as 0.02 wt%) could reduce the coefficient of friction (COF) of grease significantly. When the concentration of $\text{Mn}_3\text{O}_4\#\text{G}$ was 0.1 wt%, the COF and wear depth were 43.5% and 86.1%, lower than those of pure graphene, respectively. In addition, under the effect of friction, the microstructure of graphene in $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites tends to be ordered and normalized. Furthermore, most of the Mn_3O_4 transformed into Mn_2O_3 owing to the high temperature generated from friction. Using the Ar gas cluster ion beam sputtering method, the thickness of the tribofilm was estimated to be 25–34 nm. Finally, the improvement of the lubrication properties was attributed to the synergistic effect of the adsorbed tribofilm, i.e., the graphene island effect and the filling effect of $\text{Mn}_3\text{O}_4\#\text{G}$.

Keywords: friction; nanocomposite additive; graphene; synergistic lubrication

1 Introduction

Lubricants are widely used for reducing equipment friction and wear, thereby increasing the service life of machines, especially in heavy contact load conditions [1, 2]. More than 30% of the energy consumption of machines is related to mechanical friction and most of the mechanical failures result from wear [3, 4]. Therefore, it is crucial to improve the anti-friction and wear reduction properties of lubricants under heavy contact load [5, 6]. Ouyang et al. [7] investigated the tribological properties of three dimensional (3D) hierarchical porous graphene

as an additive in grease with three motion modes under heavy load conditions (2.55 GPa). Nehme [8] studied the tribological properties of zinc dialkyl dithiophosphates (ZDDP) with added submicron particles of titanium fluoride or iron fluoride along with polytetrafluoroethylene under heavy load condition (336 N; 2.6 GPa) and different speeds. He also investigated the wear behavior of MoS_2 grease under variable loads and speeds for extreme pressure application with a four-ball wear tester (393–786 N) [9]. Lubricating oil and grease are widely used lubricants. Although lubricating oils have excellent fluidity, which can easily induce the

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dynamic pressure effect causing the fine structure to be lubricated fully [10], the non-uniformity of the oil film prevents the further application of oils. By contrast, greases have an excellent load-carrying capacity, film formation stability, and extreme pressure performance, which are beneficial in extreme environments such as high speed, heavy load, and high-temperature environments with excessive dust [11].

Additives can effectively improve the lubrication performance of grease [12]. In particular, advanced nanoparticles have attracted considerable interest as solid additives [13–16]. Compared with disulfide materials (MoS_2 and WS_2), carbon materials have attracted increasing attention owing to their environmental friendliness and interfacial non-corrosion [17, 18]. Graphene is widely used to improve the tribological properties of lubricants owing to its excellent self-lubricating properties induced by its unique two dimensional (2D) structure [19–25]. Graphene improves the tribological performance of oils by forming a lubricating adsorption film and through the graphene interlayer slippage effect. Several studies have shown that the micromorphology of graphene plays a significant role in its lubrication properties [26, 27]. Li et al. [28] investigated the effect of the exfoliated state of graphene sheets on the lubrication and anti-friction performance. His results indicated that graphene with a loose interlayer structure and extremely low particle size can improve the tribological properties of oil effectively. By contrast, owing to the poor fluidity of grease, the lubricating effect of pure graphene as an additive in grease is less significant. Multi-layer graphene was investigated as an additive in Benton grease, and it was experimentally revealed that the coefficient of friction (COF) of the additive-incorporated grease can be reduced only slightly (8%–13%) [29]. 3D hierarchical porous graphene was synthesized by a one-step ion-exchange/activation combination method; the COF of grease added with this hierarchical porous graphene was reduced by 20% [30]. Graphene prepared by the liquid exfoliation method was shown to significantly reduce the COF by 26% under the conditions of a ball–disc contact experiment; however, the improvement in the grease carrying capacity was limited [31]. Therefore, there remains considerable scope for research on the improvement

of the tribological properties of grease by adding graphene nanoparticle additives. Moreover, the lubrication properties of graphene in grease need to be further investigated.

To further improve the performance of lubricants, hybrid graphene-based nanomaterials (Mo and W nanoparticle/graphene, MoS_2 /graphene, SiO_2 , and Si /graphene) have been synthesized and added into grease [32–35]. The synergistic effects of composite additives, such as the self-repair effect and rolling effect, can further improve the lubrication performance [36–38]. In addition, the presence of nanoparticles changes the exfoliation state and lamellar distance of graphene, making interlaminar shearing easier [34, 35]. At present, hybrid graphene-based nanomaterials are mainly synthesized using the hydrothermal method [36–40] and by functionalizing nanocores [41–43]. Solvent-free ionic nanofluids of graphene oxide-silica hybrid nanocores (GO/SiO_2) display a liquid-like behavior in the absence of any solvent and show excellent dispersion stability in base oil. However, owing to the high hardness of oxide-silica, it is easy to damage the graphene sheet structure, leading to lubrication failure [41]. Graphene oxide (GO)– TiO_2 can improve the lubrication performance of grease by forming a stable and uniform tribofilm at a high concentration of 0.5 wt% [42]. $\text{IL-GO}/\text{Cu}$ displays a lubrication performance as high as that of lubricants, but its friction load (4 N) is not sufficiently high to meet the actual operating conditions of mechanical equipment [43]. Overall, the poor lubrication performance, high additive concentration, and mild application conditions limit the further application of existing hybrid graphene-based nanomaterials as additives [41–43]. Therefore, it is necessary to develop an additive that can achieve high lubrication efficiency even under low concentrations and severe application conditions.

In our previous research, we proposed an *in situ* green method to synthesize Mn_3O_4 /graphene nanocomposites ($\text{Mn}_3\text{O}_4/\text{G}$) by introducing Mn in the synthesis process of GO. The $\text{Mn}_3\text{O}_4/\text{G}$ nanocomposite was used as an additive in the lubricating oil, and its tribological properties were investigated at a low speed (2.4 mm/s) and low load (1 GPa). The results indicated that $\text{Mn}_3\text{O}_4/\text{G}$ can considerably

improve the lubrication performance of oil [44]. However, the contact stress of actual machines under the engineering working conditions is much higher [45]. In addition, the tribological properties of this additive in grease and the performance of the composite-based grease under high-speed and heavy-load conditions have not been studied.

In this study, we investigate the lubrication properties of $\text{Mn}_3\text{O}_4/\text{G}$ as an additive in grease under high speed (80 mm/s) and heavy load (3.95–4.59 GPa). $\text{Mn}_3\text{O}_4/\text{G}$ was synthesized by an *in situ* hydrothermal method and dispersed into L-XBCEA 0 lithium grease by successive electromagnetic stirring, ultrasound vibration, and three-roll grinding. The effects of the $\text{Mn}_3\text{O}_4/\text{G}$ concentration and load condition on the tribological performance of the compound grease were investigated. Subsequently, the physical morphology and chemical composition of the wear scars after the tribology experiment were analyzed. Finally, a micro-mechanism model of anti-friction and wear reduction of $\text{Mn}_3\text{O}_4/\text{G}$ was proposed. The results of this study will provide useful information to develop an effective way to improve the lubrication performance of commercial-grade grease.

2 Experimental

2.1 Materials

Commercial grade graphite and multi-layer graphene (Com#G) were bought from Nanjing XianFeng nanotechnology Co., Ltd. Hydrogen peroxide (H_2O_2 ; 30 wt%) and sulfuric acid (H_2SO_4 ; 98 wt%) were purchased from Shanghai Titan Technology Co.,

Ltd. Potassium permanganate (KMnO_4) and potassium hydroxide (KOH) were supplied by Guangzhou Helong Chemical Co., Ltd. Deionized water and petroleum ether were provided by Nantong Runfeng Petrochemical Co., Ltd. L-XBCEA 0 lithium grease was obtained from China Great Wall Lubricants Co., Ltd.

2.2 Synthesis of $\text{Mn}_3\text{O}_4/\text{G}$ nanoparticles and $\text{Mn}_3\text{O}_4/\text{G}$ grease

2.2.1 Synthesis of $\text{Mn}_3\text{O}_4/\text{G}$

$\text{Mn}_3\text{O}_4/\text{G}$ was synthesized *in situ* using a hydrothermal method [44], following the process shown in Fig. 1. First, 10.0 g of KMnO_4 particles were gradually added to 300 mL of H_2SO_4 (98 wt%) solution in an ice bath. Subsequently, 45.0 g of commercial graphite was added into the mixed solution slowly and uniformly. Second, slow electromagnetic stirring was performed to mix the solid particles uniformly. Subsequently, 1,000 mL of deionized water was added into the mixture; after that, the mixture was heated in a water bath at 45 °C and held for 60 min to completely oxidize the graphite. Third, 50 mL of H_2O_2 (30 wt%) solution was added to the mixture at a uniform rate, which gradually changed the mixture color from dark brown to golden. Next, the mixture was stirred for 30 min. Fourth, approximately 500 g of flake KOH was slowly added to the mixed liquid until the pH value of the mixture became greater than 8.0. The mixture was then filtered through suction, and the filtered product was dried at 180 °C for 6 h to fully reduce the GO; the dried matter was then dissolved with deionized water. Subsequently, the solution was filtered again, and the filtered product was dried

Fig. 1 Flowchart of the synthesis and preparation process of $\text{Mn}_3\text{O}_4/\text{G}$ nanocomposites and $\text{Mn}_3\text{O}_4/\text{G}$ grease.

at 80 °C for 2 h. This step was repeated three times to completely remove soluble impurities. Finally, approximately 6 g of rough solid powder of $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites was obtained.

2.2.2 Preparation of $\text{Mn}_3\text{O}_4\#\text{G}$ grease

The preparation process of $\text{Mn}_3\text{O}_4\#\text{G}$ grease is also illustrated in Fig. 1. First, the rough $\text{Mn}_3\text{O}_4\#\text{G}$ powder was processed by ball milling to obtain a uniformly refined powder. Second, different amounts of refined $\text{Mn}_3\text{O}_4\#\text{G}$ powder were added to 10.0 g of pure L-XBCEA 0 lithium grease to obtain different additive concentrations of compound grease (0.02 wt%, 0.03 wt%, 0.05 wt%, 0.1 wt%, and 0.5 wt%). Subsequently, each grease sample was dissolved with 15 mL of petroleum ether, and the mixture was stirred manually until its observed color was uniform. Next, the mixture was stirred electromagnetically in a water bath at 50 °C for 180 min until the petroleum ether was completely evaporated. Subsequently, to make the compound grease uniform at the micro-level, it was subjected to ultrasonic vibration for 30 min. Finally, the compound grease was refined three times using a three-roll milling machine (YS65 Shanghai Yongyan Nano Technology Co., Ltd.). Finally, we obtained $\text{Mn}_3\text{O}_4\#\text{G}$ grease with different additive concentrations (Fig. 2).

Fig. 2 Digital photographs of $\text{Mn}_3\text{O}_4\#\text{G}$ greases with different concentrations of $\text{Mn}_3\text{O}_4\#\text{G}$ additive: (a) P.G.; (b) P.G. + 0.02 wt% $\text{Mn}_3\text{O}_4\#\text{G}$; (c) P.G. + 0.03 wt% $\text{Mn}_3\text{O}_4\#\text{G}$; (d) P.G. + 0.05 wt% $\text{Mn}_3\text{O}_4\#\text{G}$; (e) P.G. + 0.1 wt% $\text{Mn}_3\text{O}_4\#\text{G}$; (f) P.G. + 0.5 wt% $\text{Mn}_3\text{O}_4\#\text{G}$.

2.3 Tests of tribological properties

To investigate the tribological properties of $\text{Mn}_3\text{O}_4\#\text{G}$ as an additive in L-XBCEA 0 lithium grease, tribology tests were conducted on the SRV4 tester (Optimol Instruments, Germany). The friction pairs were in a ball–disc contact form and the material of both upper and lower parts of the friction pair was GCr15 with a hardness of approximately 650–700 HV [26]. In addition, the tribological properties of pure grease (P.G) and the grease containing commercial graphene (Com#G) were investigated for comparison.

2.3.1 Investigation of the optimum concentration of $\text{Mn}_3\text{O}_4\#\text{G}$

According to previous studies, the concentration of additives greatly affects the tribological properties of grease. The tribological properties of grease with different additive concentrations under the same experimental conditions were investigated to determine the optimal concentration of $\text{Mn}_3\text{O}_4\#\text{G}$ additives. Table 1 lists the specific experimental conditions.

2.3.2 Comparative experiments with commercial graphene (Com#G) additive

To further illustrate the excellent tribological properties of $\text{Mn}_3\text{O}_4\#\text{G}$ as an additive, we compared the properties of commercial graphene. The compound grease containing Com#G with different concentrations was prepared through the same process used for the preparation of the $\text{Mn}_3\text{O}_4\#\text{G}$ grease, which was described in Section 2.2.2. Further, the tribological properties of Com#G were investigated under the experimental conditions described in Section 2.3.1 (Table 2).

2.3.3 Effect of load factor on the tribological properties of $\text{Mn}_3\text{O}_4\#\text{G}$

After determining the relative optimal concentration of $\text{Mn}_3\text{O}_4\#\text{G}$, the effect of the load factor on the tribological properties of $\text{Mn}_3\text{O}_4\#\text{G}$ was investigated by varying the load conditions from 600 to 900 N at 50 N-intervals. Table 3 lists the detailed experimental conditions.

Table 1 Experimental conditions for the investigation of $\text{Mn}_3\text{O}_4/\text{G}$ concentrations.

Test sample	Load (N)	Stroke (μm)	Temperature ($^{\circ}\text{C}$)	Frequency (Hz)	Time (s)
P.G					
P.G + 0.02 wt% $\text{Mn}_3\text{O}_4/\text{G}$	700	2,000	25	20 (80 mm/s)	1,800
P.G + 0.03 wt% $\text{Mn}_3\text{O}_4/\text{G}$					
P.G + 0.05 wt% $\text{Mn}_3\text{O}_4/\text{G}$					
P.G + 0.1 wt% $\text{Mn}_3\text{O}_4/\text{G}$					
P.G + 0.5 wt% $\text{Mn}_3\text{O}_4/\text{G}$					

Table 2 Experimental conditions for the investigation of Com#G concentrations.

Test sample	Load (N)	Stroke (μm)	Temperature ($^{\circ}\text{C}$)	Frequency (Hz)	Time (s)
P.G + 0.02 wt% Com#G	700	2,000	25	20 (80 mm/s)	1,800
P.G + 0.03 wt% Com#G					
P.G + 0.05 wt% Com#G					
P.G + 0.1 wt% Com#G					
P.G + 0.5 wt% Com#G					

Table 3 Experimental conditions for the investigation of the contact loads.

Test sample	Load (N)	Stroke (μm)	Temperature ($^{\circ}\text{C}$)	Frequency (Hz)	Time (s)
P.G P.G + 0.1 wt% $\text{Mn}_3\text{O}_4/\text{G}$	600	2,000	25	20 (80 mm/s)	1,800
	650				
	700				
	750				
	800				
	850				
	900				

2.3.4 Estimation of contact stress

According to our previous study, the load conditions (1 GPa) considerably affect the COF and wear of compound grease [44]. However, we must verify this result at higher load conditions. For this purpose, we calculated the maximum Hertz contact stress from the Hertz stress formula [7]. Table 4 shows the calculation results of the Hertz contact stress under different load conditions.

Table 4 Calculation results of Hertz contact stress under different contact load conditions.

Load(N)	600	650	700	750	800	850	900
Contact stress (GPa)	3.95	4.12	4.22	4.32	4.41	4.50	4.59

2.4 Characterization

The micromorphology of $\text{Mn}_3\text{O}_4/\text{G}$ nanosheets was characterized by environmental scanning electron microscopy (ESEM; FEI Quanta 200 FEG, Netherlands) and high-resolution transmission electron microscopy (TEM; JEM-2010, Japan) with an accelerating voltage of 120 kV. The surface distribution of Mn was determined by energy dispersive spectroscopy (EDS; Oxford X-MaxN, England) with an accelerating voltage of 15 kV. The crystal lattice structure and the orientation were identified by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer (Bruker, USA). The Raman spectra of $\text{Mn}_3\text{O}_4/\text{G}$ were obtained with a Jobin-Yvon LabRam HR800 confocal Raman system with 632.8 nm diode laser excitation at -70°C . The structure and valence of elements were analyzed

by X-ray photoelectron spectroscopy (XPS) using the EscaLab 250Xi X-ray photoelectron spectroscope (Thermo Fisher, USA). The tribofilm thickness was estimated using Ar-ion sputtering (Thermo Fisher, USA). The 3D morphology of the wear scars was measured using a 3D white-light interferometer (ContourGT-K1 Bruker, USA). In addition, the optical morphology of wear scars was observed using an optical microscope (VH-5000 from Keyence, Japan).

3 Results and discussion

3.1 Characterization results

Figure 3 shows the XRD pattern of the $\text{Mn}_3\text{O}_4\#\text{G}$ powder. It can be seen that the characteristic diffraction peak is consistent with that of the standard Mn_3O_4 spectrum, i.e., $2\theta = 18.022^\circ$, 28.927° , 32.394° , 36.102° , and 59.937° [46]. Simultaneously, the singular peak at $2\theta = 26.152^\circ$ illustrates that a small amount of $\text{MnO}(\text{OH})$ exists in $\text{Mn}_3\text{O}_4\#\text{G}$, which is consistent with our previous results [44].

Figure 4 shows SEM and TEM images of the micromorphology of $\text{Mn}_3\text{O}_4\#\text{G}$. From Fig. 4(a), it can be seen that the size of the $\text{Mn}_3\text{O}_4\#\text{G}$ flakes is uniform. Figure 4(b) shows that the size of a single $\text{Mn}_3\text{O}_4\#\text{G}$ flake that did not go through the ball milling process is approximately 8–10 μm . This unique lamellar structure causes an easy interlayer slip of graphene flakes, which improves the tribological properties of $\text{Mn}_3\text{O}_4\#\text{G}$ grease. Figures 4(c) and 4(d)

Fig. 3 XRD pattern of $\text{Mn}_3\text{O}_4\#\text{G}$ powder and standard spectra of Mn_3O_4 and $\text{MnO}(\text{OH})$.

Fig. 4 Characterization of $\text{Mn}_3\text{O}_4\#\text{G}$ nanoparticles: (a) SEM image $\times 300$; (b) SEM image $\times 3,000$; (c) EDS image of carbon; (d) EDS image of manganese; (e) TEM image $\times 20,000$; (f) TEM image $\times 200,000$.

show the EDS surface distribution images of C and Mn, respectively, in a single $\text{Mn}_3\text{O}_4\#\text{G}$ flake shown in Fig. 4(b). The obvious physical boundaries of the $\text{Mn}_3\text{O}_4\#\text{G}$ flake can be observed in Fig. 4(c). Moreover, in the area where the flake is located, the detection intensity of Mn is significantly enhanced, and Mn is uniformly distributed. Figure 4(e) and 4(f) show TEM images of $\text{Mn}_3\text{O}_4\#\text{G}$. From Fig. 4(e), it can be seen that Mn_3O_4 crystals shaped like chrysanthemums are attached to the graphene sheet. From Fig. 4(f), it can be seen that the $\text{Mn}_3\text{O}_4\#\text{G}$ flakes have a regular edge.

The dispersion uniformity of additives significantly affects the tribological properties of the compound grease. To detect the degree of dispersion uniformity of the $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites in the base grease, EDS was performed to detect the large-scale ($450\ \mu\text{m} \times$

450 μm) dispersion of the Mn element of the compound grease. Compound grease with additive concentrations of 0.02 wt%, 0.1 wt%, and 0.5 wt% was evenly coated on quartz plates, followed by drying at 150 $^{\circ}\text{C}$ for 4 h. Figure 5 shows the SEM images of these samples. From Fig. 5, it can be seen that Mn is distributed uniformly in all three samples. Therefore, we can conclude that the $\text{Mn}_3\text{O}_4/\text{G}$ nanocomposites could be dispersed in the base grease uniformly via the method introduced in Section 2.2.2.

3.2 Tribological test results

3.2.1 Results of COF

The concentration of additives significantly affects the lubrication performance of the compound

Fig. 5 EDS images of compound grease with different concentrations of $\text{Mn}_3\text{O}_4/\text{G}$ additive: (a, b) 0.02 wt% of $\text{Mn}_3\text{O}_4/\text{G}$; (c, d) 0.05 wt% of $\text{Mn}_3\text{O}_4/\text{G}$; (e, f) 0.1 wt% of $\text{Mn}_3\text{O}_4/\text{G}$.

greases. Figure 6(a) illustrates the effect of the $\text{Mn}_3\text{O}_4/\text{G}$ concentration on the COF at a load of 700 N and a temperature of 25 $^{\circ}\text{C}$. It can be seen that $\text{Mn}_3\text{O}_4/\text{G}$ has the characteristics of “trace but efficient”, and reduces the COF of the compound grease from 0.193 to 0.131 at a concentration as low as 0.02 wt%. However, the anti-friction effect is unstable at low-concentrations of $\text{Mn}_3\text{O}_4/\text{G}$ additives (0.02 wt%, 0.03 wt%, and 0.05 wt%). The compound grease containing 0.02 wt%, 0.03 wt%, and 0.05 wt% $\text{Mn}_3\text{O}_4/\text{G}$ nanocomposites appears unstable after lubrication tests with durations of 900, 1,000, and 1,600 s, respectively. Nevertheless, low-concentration additives can still achieve significant anti-friction effects. Relative to P.G, when the $\text{Mn}_3\text{O}_4/\text{G}$ additive concentration reaches 0.1 wt%, the COF decreases from 0.193 to 0.109 (43.5%), which indicates a relatively high anti-friction effect. Furthermore, at this concentration, the compound grease achieves a super-stable state, i.e., the COF does not fluctuate even up to 1,400 s. For comparison, the COF of P.G with 0.1 wt% Com#G was also investigated. It can be seen that the addition of

Fig. 6 COF of grease with different concentrations of additive: (a) COF of grease with different concentrations of the $\text{Mn}_3\text{O}_4/\text{G}$ additive as a function of time; (b) average COF of $\text{Mn}_3\text{O}_4/\text{G}$ grease and Com#G grease as a function of the additive concentration; (c) average COF of P.G and P.G + 0.1 wt% $\text{Mn}_3\text{O}_4/\text{G}$ as a function of contact load.

Com#G reduces the COF only slightly (9.3%). However, when the concentration of $\text{Mn}_3\text{O}_4\#G$ is greater than 0.1 wt% (i.e., 0.5 wt%), the tribological properties of compound grease degrade. Owing to the high concentration of additives, $\text{Mn}_3\text{O}_4\#G$ nanocomposites are more likely to agglomerate during the friction process, which makes it difficult for $\text{Mn}_3\text{O}_4\#G$ to enter the tribological contact area, resulting in poor lubrication properties.

In addition, to verify the potential application of $\text{Mn}_3\text{O}_4\#G$, some comparative experiments with commercial graphene were conducted. Figure 6(b) shows the comparative experiment results of $\text{Mn}_3\text{O}_4\#G$ and Com#G under a load of 700 N at a temperature of 25 °C; the average COF is the average of three consecutive experiments. It can be seen that the addition of $\text{Mn}_3\text{O}_4\#G$ greatly reduces the average COF of the compound grease, even at a super-low concentration. On the contrary, the addition of Com#G at all five concentration levels does not significantly reduce the average COF of the compound grease. Moreover, the average COF is even higher than that of P.G when 0.03 wt% Com#G is added in the grease, and the average COF of $\text{Mn}_3\text{O}_4\#G$ is more stable than that of Com#G, as indicated by the error bars.

The load conditions also have a significant influence on the lubrication characteristics of $\text{Mn}_3\text{O}_4\#G$ additives. Figure 6(c) shows the tribological properties of grease at a load varying from 600 to 900 N at 50 N-intervals. As the load increases, the compound grease containing 0.1 wt% $\text{Mn}_3\text{O}_4\#G$ maintains a relatively stable average COF (0.11–0.12). On the contrary, the average COF of P.G fluctuates greatly with a gradual decreasing tendency (0.14–0.18). When the load is lower than 750 N, $\text{Mn}_3\text{O}_4\#G$ reduces the average COF by approximately 37.1%. However, the reduction in the average COF gradually decreases at loads higher than 750 N.

In conclusion, the trace amount of $\text{Mn}_3\text{O}_4\#G$ (as low as 0.02 wt%) significantly reduced the COF of grease. A relatively optimal anti-friction effect (43.5%) was obtained when the concentration of $\text{Mn}_3\text{O}_4\#G$ additive was 0.1 wt%. Compared with Com#G, $\text{Mn}_3\text{O}_4\#G$ considerably improved the lubrication

performance of the grease. Furthermore, when the load was lower than 750 N, the tribological properties of grease improved more prominently.

3.2.2 Results of wear and scar

The micromorphology of the wear scars of the compound grease with the $\text{Mn}_3\text{O}_4\#G$ additives under 700 N was characterized by a 3D white-light interferometer, and the results are shown in Fig. 7. Figure 8 shows the 2D cross-sectional morphology of each wear and scar. With the gradual increase in the concentration of $\text{Mn}_3\text{O}_4\#G$, the depth and width of the corresponding wear scar gradually decrease. At a concentration of 0.1 wt%, a relatively optimal wear reduction effect is obtained; compared with P.G, the scar width decreases from 1080.4 to 659.1 μm (39.0%) and the depth decreases from 9.31 to 1.29 μm (86.1%) (Table 5). However, when the additive concentration of $\text{Mn}_3\text{O}_4\#G$ exceeds 0.1 wt%, the depth and width of the wear scar increases and the compound grease exhibits poor tribological properties. This result is consistent with the change tendency of the COF.

Fig. 7 3D micromorphology of wear scars with different concentrations of $\text{Mn}_3\text{O}_4\#G$ additive: (a) P.G; (b) P.G + 0.02 wt% $\text{Mn}_3\text{O}_4\#G$; (c) P.G + 0.03 wt% $\text{Mn}_3\text{O}_4\#G$; (d) P.G + 0.05 wt% $\text{Mn}_3\text{O}_4\#G$; (e) P.G + 0.1 wt% $\text{Mn}_3\text{O}_4\#G$; (f) P.G + 0.5 wt% $\text{Mn}_3\text{O}_4\#G$.

Fig. 8 2D profile of the cross-section of the wear scars with different concentrations of $\text{Mn}_3\text{O}_4\#\text{G}$ additive.

Furthermore, the wear spots of the spherical sample can directly reflect the lubrication performance of the greases. Figure 9 shows the intuitive characterization of the original morphology of the wear scars and wear spots. For this analysis, three concentrations of $\text{Mn}_3\text{O}_4\#\text{G}$ additives (0.0 wt%, 0.05 wt%, and 0.1 wt%) were selected. Compared with P.G, the diameter of the wear spot reduces from 1043.2 to 676.3 μm (35.2%) when 0.1 wt% of additive is added (Figs. 9(b) and 9(f)). In addition, $\text{Mn}_3\text{O}_4\#\text{G}$ significantly

alleviates the surface oxidation of the friction pairs. Under the P.G lubrication condition, severe oxidation occurs in the friction contact area with many visible furrow scratches (Fig. 9(b)). At an additive concentration of 0.05 wt%, the surface oxidation in the friction contact area is lower, but there is a large amount of burnt oxidation surface around the wear spot (Fig. 9(d)). By contrast, at the concentration of the additive of 0.1 wt%, only slight oxidation occurs on the inner and outer surfaces of the wear spot area, with the formation of small scratches (Fig. 9(f)).

3.3 Investigation of wear and scars

3.3.1 Raman spectra

Figure 10 shows the Raman spectra of the wear areas and $\text{Mn}_3\text{O}_4\#\text{G}$ powder under a similar baseline. It can be seen that the intensity and area of the G-peak on both disc and ball wear areas are significantly higher than those of the $\text{Mn}_3\text{O}_4\#\text{G}$ powder. In previous studies, it was shown that the relative intensity ratio of the D-peak and G-peak I_D/I_G reflect the order state and defect degree of graphene [47, 48].

Table 5 Wear width and depth of wear under different $\text{Mn}_3\text{O}_4\#\text{G}$ concentrations.

Concentration	0.0 wt%	0.02 wt%	0.03 wt%	0.05 wt%	0.1 wt%	0.5 wt%
Width (μm)	1080.4	935.4	686.3	713.2	659.1	682.2
Depth (μm)	9.31	5.76	3.16	3.41	1.29	3.49

Fig. 9 Optical microscope images of wear scars and wear spots under a 700 N load: (a, b) P.G; (c, d) P.G + 0.05 wt% $\text{Mn}_3\text{O}_4\#\text{G}$; (e, f) P.G + 0.1 wt% $\text{Mn}_3\text{O}_4\#\text{G}$.

Fig. 10 Raman spectra of $\text{Mn}_3\text{O}_4\#\text{G}$ powder, wear scar on the discs, and wear spot on the surface of balls.

The I_D/I_G values of the wear on the plate, ball, and $\text{Mn}_3\text{O}_4\#\text{G}$ powder were 0.844, 0.874, and 1.189, respectively. Therefore, the decrease in the I_D/I_G values of the wear on the plates and balls implied that the $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites shifted toward ordering and normalization under the effect of friction [49]. This physical effect of $\text{Mn}_3\text{O}_4\#\text{G}$ is attributed to its excellent lubrication performance.

A characteristic Raman peak of Mn_3O_4 (646 cm^{-1}) can be clearly observed in the curve of the $\text{Mn}_3\text{O}_4\#\text{G}$ powder [50]. However, Raman shifts were present in the corresponding test positions of the graphene flakes after the friction test. The main characteristic peak of the Mn element shifted from 646 to 694 cm^{-1} . That is, most of the Mn_3O_4 transformed into Mn_2O_3 under the generation of friction [51]. The internal chemical composition of Mn_3O_4 can be expressed as $\text{MnO}\cdot\text{Mn}_2\text{O}_3$. Under the action of friction, the temperature in the wear area increased sharply, causing the MnO in Mn_3O_4 to be oxidized and transformed into a more stable Mn_2O_3 form. This chemical effect of $\text{Mn}_3\text{O}_4\#\text{G}$ contributed to its excellent lubrication properties. The transformation indicated that the instantaneous temperature of the friction areas could be as high as $500\text{ }^\circ\text{C}$ [51].

3.3.2 XPS

Figure 11 shows the XPS results. A comparison of the changes in element content before and after the induction of friction indicates that the oxygen content increases sharply after friction. This is because friction generates a large amount of heat, causing the temperature in the wear scar zone to increase

rapidly. This, in turn, leads to the oxidation of the additive and the substrate. After the sample is cleaned with petroleum ether and ultrasonic waves thoroughly, a significant amount of residual Mn 2p (1.69%) is detected, indicating that a stable tribology film exists on the surface of the wear scar area. In addition, the detection signal (3.81%) of Ca 2s in the wear scar is attributed to the residual grease (Table 6).

Fig. 11 XPS full spectra with of $\text{Mn}_3\text{O}_4\#\text{G}$ powder and wear scars.

Table 6 Content of C 1s, O 1s, Mn 2p, and Ca 2s before and after friction.

Element	C 1s	O 1s	Mn 2p	Ca 2s	Summation
Before friction	58.10%	33.86%	8.04%	0.00%	100%
After friction	36.49%	58.01%	1.69%	3.81%	100%

Figure 12 shows the detailed spectra of C 1s, O 1s, and Mn 2p elements detected in the wear scar zone. C 1s has C–C, C–O, and C=O bonds (Figs. 12(a) and 12(b)) with bonding energies of 285, 288.5, and 286.8 eV, respectively [52]. Before the friction experiment, O 1s is fitted with O–C, O=C, and O–Mn bonds, and the concentration of the O–Mn bond is as high as 20.82%. However, the O 1s of the wear scar is fitted with O–C, O=C, O–Mn, and O–Fe bonds (Figs. 12(c) and 12(d)), and the concentration of the O–Mn bond decrease to 2.49%, which corresponds to the full spectrum. By contrast, the concentration of the O–Fe bond is as high as 43.3%. After the friction experiment, the Fe in the friction areas is oxidized in the substrate, leading to a sharp increase in the concentration of the O–Fe bond.

Figures 12(e) and 12(f) show that Mn 2p can be fitted into four peaks of Mn, Mn (II), Mn (III), and Mn (IV) bonds [53]. Table 7 shows the concentration of each bond. It can be seen that the intensities of Mn (II) and Mn (III) of the $\text{Mn}_3\text{O}_4\#\text{G}$ powder are 41.56% and 39.95%, respectively, and the concentration ratio of Mn (II) and Mn (III) $C_{\text{Mn(II)}}/C_{\text{Mn(III)}}$ is 1.04. By contrast, after the friction experiment, the concentration of Mn (II) and Mn (III) is 10.73% and 76.01%, respectively (Table 7), and the $C_{\text{Mn(II)}}/C_{\text{Mn(III)}}$ ratio

decreases to 0.14. Furthermore, the concentration of Mn decreases from 9.26% to 3.74% after the friction experiment. However, there is no significant change in the Mn (IV) concentration, which implies that almost all of the Mn and Mn (II) transformed into Mn (III) under friction induction. That is, most of the MnO in Mn_3O_4 converted into Mn_2O_3 , which is consistent with the Raman shift of Mn_3O_4 .

3.3.3 Ar gas cluster ion beam sputtering

Tribofilms are useful to control the friction and wear of tribological pairs. In the friction contact area, the tribofilm can effectively separate the two tribological surfaces, avoiding the direct contact of rough peaks, thus improving the anti-friction and anti-wear properties [54, 55].

Figure 13 shows the results of Ar gas cluster ion beam sputtering, which was conducted to verify the existence and estimate the thickness of the tribofilm in the friction area of the disc. Eleven sputtering rounds were performed with a single step sputtering depth of 3.1 nm. After each sputtering, XPS narrow-spectrum detection was conducted to detect the elemental distribution at the corresponding depth. From Fig. 13(a), it can be seen that as the sputtering depth increases, the detection intensity

Fig. 12 XPS narrow spectra of typical elements of $\text{Mn}_3\text{O}_4\#\text{G}$ powder and wear scars: Narrow spectra of C 1s (a) before and (b) after friction, O 1s (c) before and (d) after friction, and Mn 2p (e) before and (f) after friction.

Table 7 Content of Mn(II), Mn(III), Mn(IV), and Mn before and after friction.

Sample	Mn(II)	Mn(III)	Mn(IV)	Mn	Summation
Before friction	41.55%	39.95%	9.24%	9.26%	100%
After friction	10.73%	76.01%	9.52%	3.74%	100%

of O 1s slowly decreases. This means that the content of the oxygen element decreases gradually. After sputtering for eight times, the detection intensity of the oxygen element tends to be stable (No.09, No.10, and No.11), which indicates that the sputtering ion beam has been applied to the lower substrate. In addition, the same test intensity variation trend can be reflected in the Mn 2p element detection (Fig. 13(b)). After sputtering for nine times, the characteristic peak of Mn 2p is so weak that it can

hardly be detected (No.10 and No.11). Hence, the thickness of the tribofilm is estimated to be 25–34 nm.

3.4 Mechanism of lubrication

To reveal the anti-friction and wear-reduction mechanism of $\text{Mn}_3\text{O}_4/\text{G}$, the wear scars of the compound grease with 0.1 wt% $\text{Mn}_3\text{O}_4/\text{G}$ additive at loads of 600, 700, 800, and 900 N were observed under the optical microscope, and the results are shown Fig. 14. It can be seen that some island-shaped black areas are distributed on the surface of all the wear scars evenly (Figs. 14(b), 14(d), 14(f), and 14(h)). The Raman spectra (Fig. 10) indicate that these areas are the $\text{Mn}_3\text{O}_4/\text{G}$ flakes attached to the surface of the wear scar. In addition, a relatively small $\text{Mn}_3\text{O}_4/\text{G}$ flake can fill the scratch grooves directly, thus inhibiting the further expansion of the scratches.

Fig. 13 Ar gas cluster ion beam sputtering results. Gradient sputtering results of (a) O 1s and (b) Mn 2p. **Fig. 14** Optical microscope images of wears under different load conditions: (a, b) 600 N; (c, d) 700 N; (e, f) 800 N; (g, h) 900 N.

Fig. 15 Schematic of the lubrication mechanism of $\text{Mn}_3\text{O}_4\#\text{G}$ as an additive in grease during the friction experiment.

From all the examination and characterization results described above, the lubrication mechanism of the $\text{Mn}_3\text{O}_4\#\text{G}$ compound grease can be proposed as follows: The improvement of the lubrication properties can be attributed to the synergistic effect of the tribofilm formed by the $\text{Mn}_3\text{O}_4\#\text{G}$ compound grease, i.e., the graphene island effect and filling effect of the $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites (Fig. 15). Under high speed (80 mm/s) and heavy load (3.95–4.59 GPa) experimental conditions, the grease formed a stable tribofilm on the surface of the wear scar area; this resulted in the isolation of most of the friction contact areas, and thus, the direct contact of friction pairs was avoided.

Furthermore, under the reciprocating friction motion, $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites adhered to the surface of the wear scar area to form graphene islands. On the one hand, the presence of graphene islands can improve the strength of the tribofilm; this will increase the load-carrying capacity of the tribofilm [56, 57]. On the other hand, interlaminar shearing occurs between graphene sheets, which will reduce the COF and improve the anti-friction properties. In this process, Mn_3O_4 serves as an interlayer lubricant, which reduces the slipping energy barrier between the graphene layers, thus decreasing the COF [33, 34, 41]. In addition, the filling effect of the small size of $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites can prevent the further expansion of the scars, thus improving the anti-wear properties of the compound grease.

4 Conclusions

$\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites were synthesized using an *in situ* hydrothermal methods. $\text{Mn}_3\text{O}_4\#\text{G}$ compound grease was prepared by successive electromagnetic stirring, ultrasound vibration, and three-roll grinding. The micromorphology of $\text{Mn}_3\text{O}_4\#\text{G}$ was characterized by ESEM, EDS, and TEM methods. In addition, the tribological properties of the compound grease were investigated in detail. The conclusions can be summarized as follows:

1) $\text{Mn}_3\text{O}_4\#\text{G}$ can achieve excellent lubrication effect even at super-low concentration (0.02 wt%) under high-speed (80 mm/s) and heavy-load (3.95–4.95 GPa) conditions. The COF and wear depth can be reduced by 43.5% and 86.1% under the relative optimum concentration of 0.1 wt%. Furthermore, when the load is lower than 750 N, the tribological properties of grease improve more prominently.

2) The microstructure of graphene in $\text{Mn}_3\text{O}_4\#\text{G}$ nanocomposites tends to become ordered and normalize under the effect of friction. Therefore, the physical effect of $\text{Mn}_3\text{O}_4\#\text{G}$ is beneficial to increase the lubrication performance. The temperature increases sharply under friction, converting most of the MnO in Mn_3O_4 into a more stable form of Mn_2O_3 , improving the adsorption stability of the nanocomposites on the friction interfaces. Therefore, the chemical effect of $\text{Mn}_3\text{O}_4\#\text{G}$ is also beneficial to increase the lubrication performance.

3) The lubrication mechanism of the compound grease can be described by the synergistic effect of the adsorbed tribofilm, i.e., the graphene island effect and filling effect. Most of the friction contact areas are covered by the tribofilm; thus, the direct contact of friction pairs is avoided. The graphene islands can enhance the strength of the tribofilm and cause interlaminar slipping, thereby reducing the COF and improving the anti-friction properties. In addition, the filling effect prevents further expansion of wear scars, thus enhancing the anti-wear properties of the compound grease.

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